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PHOTODISSOCIATION SPECTROSCOPY OF CO_3^{-*}

Prepared by

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The photodissociation cross section of the carbon trioxide negative ion has been measured over the wavelength range from 457.9 nm to 694.0 nm, and reveals detailed structure reflecting the vibrational spacings of the predissociating excited electronic state. From an analysis of the structure, we identified three vibrational modes of the excited state having energies of 990 cm(-1), 1470 cm(-1), and 880 cm(-1). The bond energy of the carbon trioxide negative ion (to separation into a carbon dioxide molecule and an atomic oxygen negative ion) was

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determined to be 1.8 ± 0.1 eV, and the electron affinity of carbon trioxide was found to be 2.9 ± 0.3 eV. By comparison with theoretical calcuations, the lowest predissociating state was identified as the one doublet A one state. Observations regarding other excited states of the carbon trioxide negative ion are made.

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I. INTRODUCTION

The negative ion CO_3^- is believed to be important in the ion chemistry of the D region[1,2] of the ionosphere and in CO_2 lasers.[3] This ion has been studied in the solid state both in $KHCO_3$ crystals[4-6] and in an argon matrix.[7] Walsh,[8] in his classic series of papers on molecular geometry, discussed the expected electron configuration and geometry of CO_3^-. Olsen and Burnelle[9] have made theoretical calculations of the geometry and electronic structure of the ground and lower excited states of this ion. The formation of the ion in the gas phase has been studied using drift tube mass spectrometers[10-13] and a flowing afterglow.[14] Two measurements[15,16] of the photodetachment of CO_3^- have been recently reported. In our studies of the photodissociation of CO_3^- in the gas phase,[17,18] we have observed behavior apparently characteristic of a predissociating excited state. In this paper we present the results of a more detailed experimental investigation of this state, and attempt to find the description of CO_3^- most consistent with all the available evidence.

The experiments were performed using a drift tube mass spectrometer,[17,18] an argon-ion laser, and a tunable dye laser. The CO_3^- ions, formed by reaction between O^- and CO_2, drift under the influence of a weak applied electric field toward an extraction aperture. The pressure of the CO_2 gas in the drift region was typically 0.050 torr for these experiments. The ratio of

the electric field strength to the neutral-gas density, E/N, was chosen so that the directed drift velocity was only about one-tenth the mean thermal speed of the ions and gas molecules at room temperature. Thus, the ions experience many thermalizing collisions following their production. Just before passing through the extraction aperture, the ions intersect the intracavity photons of the dye laser, which is chopped at 100 Hz. The ions that pass through the extraction aperture are mass selected by a quadrupole mass spectrometer and individually detected by an electron multiplier. By counting these ions for alternate periods when the laser is on and off, we can determine the cross section for the loss of a particular ion species due to photon interaction, i.e., the total photodestruction cross section. Tuning the mass spectrometer to the appropriate mass permits identification of photofragment ions resulting from the photodissociation.

II. PHOTODISSOCIATION SPECTRUM

We have measured the absolute photodestruction cross section for the process

$$CO_3^- + h\nu \rightarrow CO_2 + O^- \qquad (1)$$

using continuously tunable radiation with a 0.5 Å bandwidth over the range from 6940 to 5270 Å, and at seven discrete wavelengths of the argon-ion laser between 5287 and 4579 Å. This cross section is presented in Fig. 1

as a function of photon energy. Some of these results were presented in Refs. 17 and 18, where we discussed in some detail experimental tests which established that the only important destruction process occurring is the single photon photodissociation represented by Eq. (1). Thus, photodetachment, multiple photon processes, and collisional dissociation or detachment do not contribute significantly to the cross section presented in Fig. 1. If the CO_3^- ions in reaction (1) have a thermal distribution of internal states, the structure observed in Fig. 1 should reflect transitions to various vibrational modes of one or more predissociating CO_3^- electronic states.

In earlier work,[17,18] we were able to conclude that the effect of vibrational excitation in the reactant CO_3^- molecule on either the magnitude or shape of the cross section was negligible at photon energies above 1.94 eV. Near the threshold for dissociation, however, the cross section should be particularly susceptible to any contributions from vibrational excitation in the CO_3^- at the time of photon absorption. The peaks in Fig. 1 near 1.80 and 1.85 eV might be especially suspected of originating from excited CO_3^- since they occur at relatively low photon energies. Unfortunately, the poorly defined peak near 1.80 eV could not be studied in detail owing to the small size of its cross section and the lack of photon intensity at these energies. The cross section at this energy may therefore originate from vibrationally excited CO_3^-. However, detailed studies of the peaks at 1.85 eV and higher energies, which are discussed

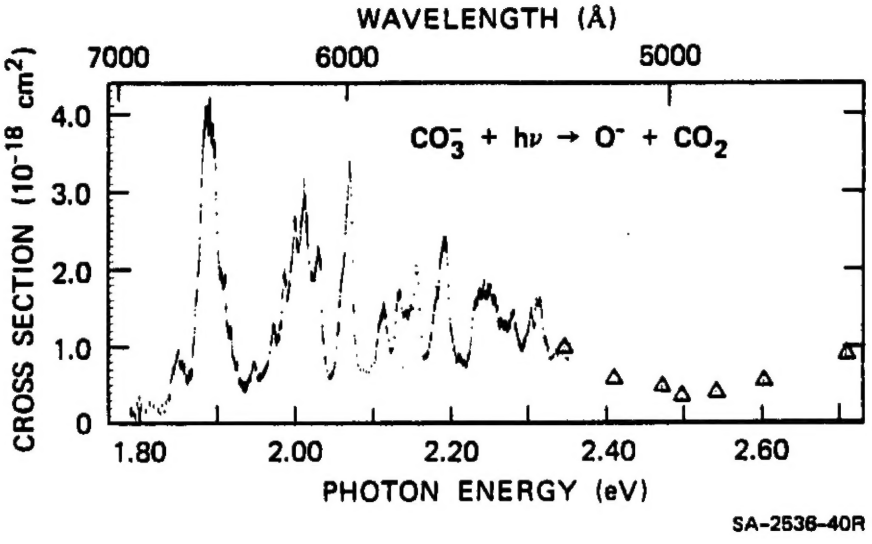

Figure 1. Photodissociation cross section of CO_3^- as a function of both photon energy and wavelength. The data shown as points were obtained using a tunable dye laser with a resolution of approximately 0.5 Å. The triangles are data taken at the discrete lines of the argon ion laser.

in the remainder of this section, show clearly that the main structure in Fig. 1 originates from ions in their ground vibrational levels.

The parent CO_3^- is formed by the reaction

$$O^- + 2CO_2 \rightarrow CO_3^- + CO_2 \quad . \tag{2}$$

We have previously[17] observed variations in the magnitude of the photodissociation cross section at 2.41 eV (5145 Å), which we attributed to vibrational excitation in the initial production of CO_3^- and to an increase in the photodissociation cross section at this energy with increasing vibrational excitation of the CO_3^- ion. We further showed that, at a CO_2 pressure of 0.050 torr, an E/N of 10 Td (1 Td = 10^{-17} V cm^2), and a drift distance of 10 cm or greater, the photodissociation cross section was constant, indicating that the initial vibrational excitation had been relaxed through collisions with the CO_2 molecules in the drift region. Thus, under these conditions, the ions were essentially in thermal equilibrium with the gas molecules at room temperature.

If the photoabsorption occurring at 1.85 eV (6700 Å) originates from an excited level of the ground state, we would expect the observed photodissociation cross section in the region of this peak to increase under conditions that favored higher vibrational excitation in the ground state. One such condition is a short drift distance, so that the vibrationally excited CO_3^- ions produced by reaction (2) have fewer deexciting collisions before entering the laser beam. The cross section at 1.85 eV was measured for drift distances from 5 to 30 cm. Over this

range the number of collisions that a CO_3^- ion formed in the source underwent before intersecting the photon beam varied from approximately 200 to 1200. The actual increase was even greater, since for a drift distance of 5 cm approximately half the CO_3^- ions intersecting the laser beam are formed outside the source along the drift path preceding the laser beam, while for a drift distance of 30 cm essentially all the observed CO_3^- ions are formed 20 cm or more away from the laser beam. At 2.41 eV, under these same conditions, we observed a cross section for a 5-cm drift distance that was about 50% greater than that for a 15-cm drift distance. At 1.85 eV, however, no variation was observed in the cross section with drift distance, indicating either that this peak does not originate from a vibrationally excited level or that the collisional deexcitation cross section for such an excited level is less than 10^{-18} cm^2. Reasons for the apparent dependence of the cross section at 2.41 eV on the vibrational temperature of the CO_3^- ground state are not yet understood, but they do not affect the conclusions of this paper.

A second condition for enhancing the vibrational excitation in a CO_3^- ion when it interacts with the laser is to increase E/N in the drift region so that the ions have a mean kinetic energy[19] substantially above thermal ($300^{\circ}K$) energy. This should have two effects: the deexcitation of any vibrational excitation produced in the formation of the CO_3^- may be reduced, and the increased average collision energy should enhance the parent ion vibrational excitation. Thus an increase in E/N will tend to

increase the temperature of the ions, although it is unlikely that the kinetic, vibrational, and rotational energies at any high E/N can be described by a single temperature. The photodissociation cross section at 1.85 eV was measured for E/N values from 10 to 150 Td, corresponding to mean center-of-mass kinetic energies ranging from essentially thermal energy (0.4 eV) to 0.13 eV, as calculated from the measured drift velocities using the Wannier relation.[19] At the higher E/N values, collisions between CO_3^- and CO_2 were energetic enough to cause substantial vibrational excitation of the CO_3^-. At 2.41 eV (5145 Å), we again observed[17] a significant increase in the photodissociation cross section over this range of E/N. However, at 1.85 eV the cross section was observed to remain constant over this entire range of E/N values.

Thus, the photodissociation cross section at 1.85 eV appears to be independent of both the number of collisions and their energy, under conditions where significant dependencies were observed at 2.41 eV. This independence strongly indicates that the peak at 1.85 eV does not originate from a vibrationally excited level of the parent CO_3^-.

III. VIBRATIONAL FREQUENCIES OF THE EXCITED STATE

The complexity of the structure and the close spacing of the peaks shown in Fig. 1 indicate that the transitions observed are to vibrational levels above the ground vibrational level of the excited electronic state. It can further be deduced that, near the dissociation energy of CO_3^-,

substantial vibrational excitation of the excited state is needed to facilitate the dissociation.

Experiments in $KHCO_3$ crystals[4-6] and in an argon matrix[7] have concluded that the ground state CO_3^- in these environments has C_{2v} symmetry, as shown in Fig. 2. Calculations for the free ion[9] also predict a C_{2v} geometry, with the unique angle α less than 120°. At the threshold for dissociation, this molecule must break up into O^- and CO_2, with no excess kinetic or internal energy. The energy required to dissociate CO_3^- directly into O^- and CO_2 bent at 120° has been calculated[20] to be between 1.2 and 2.5 eV greater than the adiabatic dissociation threshold at which the CO_2 fragment is produced in its linear ground state. Consequently, over the range of measurements presented in Fig. 1, the dissociation of CO_3^- requires a substantial change in the geometry of the molecular ion. Such a change could result from the excitation of bending mode vibrations in the excited electronic state.

We therefore searched for vibrational spacings characteristic of the excited state that could explain the observed structure. The search was confined to the range 500 to 2500 cm^{-1}, since vibrational spacings for similar molecules[21] lie in this range. It was found that three frequencies, 990 cm^{-1}, 1470 cm^{-1}, and 880 cm^{-1}, give reasonable identifications of nearly all the observed peaks if the ground vibrational level of the excited electronic state is assumed to be 1.520 ± 0.002 eV (12260 ± 10 cm^{-1}) above the ground level of the ground state. The peaks in Fig. 3 identified

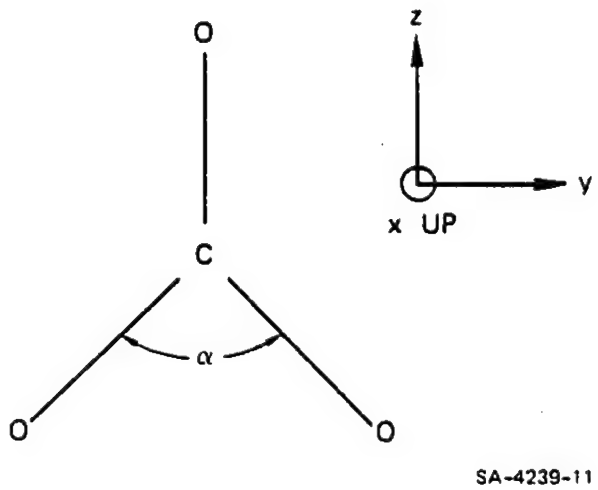

Figure 2. Geometry of the ground state CO_3^- ion having C_{2v} symmetry, showing the orientation of its coordinate system.

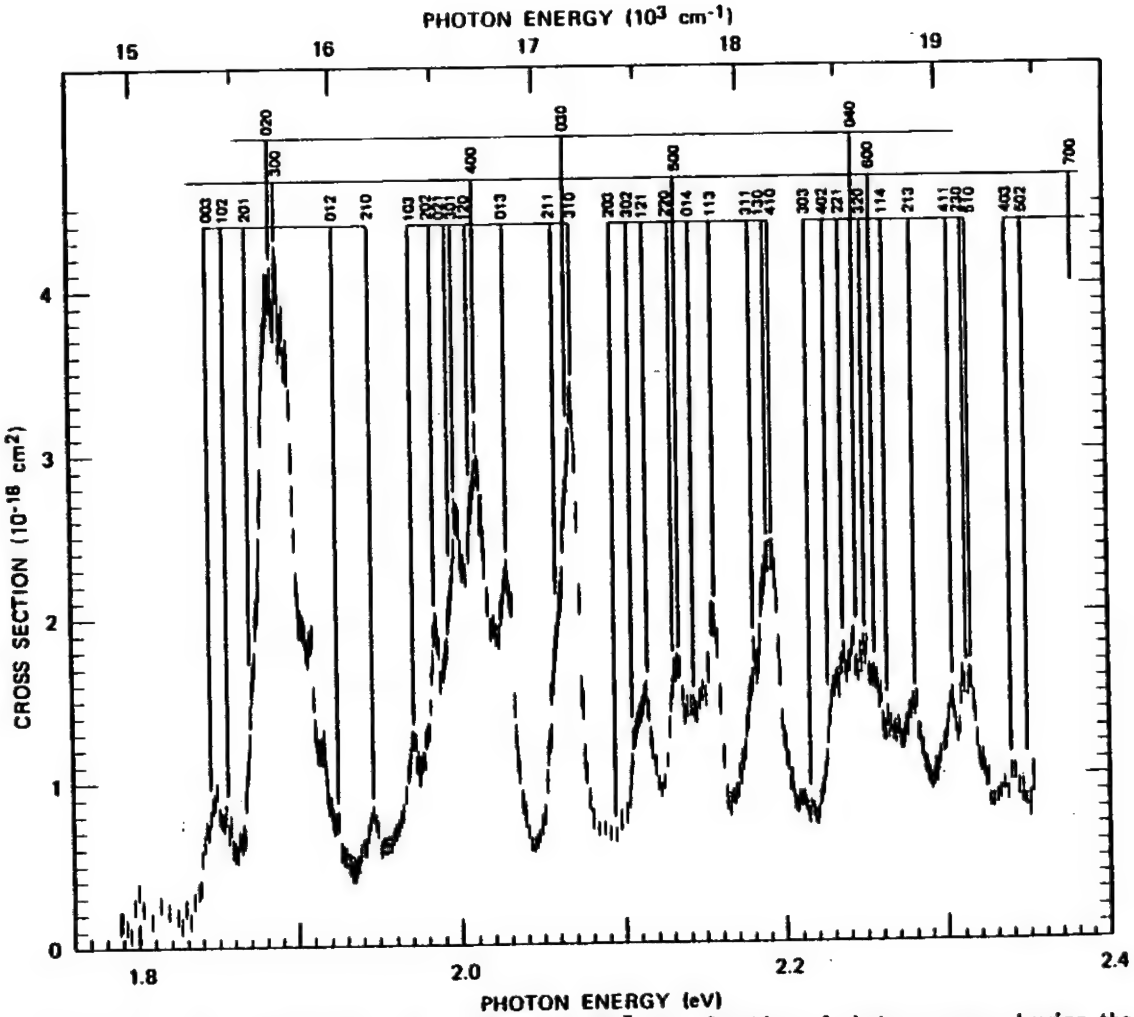

Figure 3. Photodissociation cross section of CO_3^- as a function of photon energy showing the assignment of transitions to three vibrational modes of the 1^2A_1 excited state from the ground vibrational levels of the 1^2B_2 state. The origin of the 1^2A_1 state is at 1.520±0.002 eV, and the vibrational modes are found to have frequencies of 990, 1470, and 880 cm^{-1}, respectively.

according to this scheme are labelled with a set of three numbers, ijk, indicating i units of the 990 cm^{-1} vibration, j of the 1470 cm^{-1} vibration, and k of the 880 cm^{-1} vibration. The spectrum can be viewed as a series of groups, each subsequent group obtained by adding 990 cm^{-1} to the energy of each peak in the preceding group. Superimposed on this is a progression in the 1470 cm^{-1} vibration. The small peak at 1.80 eV and the structure on the side of the large peak at 1.89 eV are not explained by this scheme, but may arise from other vibrational levels of the excited state or from vibrationally excited levels of the ground state, as mentioned earlier.

It is difficult to identify these vibrational spacings with any specific three of the six vibrational modes of CO_3^-. However, since dissociation near the threshold requires such a large change in the angle α, it is suggested that all these vibrational spacings correspond to bending modes of the excited state. We have studied selected regions of the $^{13}CO_3^-$ photodissociation spectrum and find only a small isotope shift (9 ± 3 cm^{-1} per vibrational quantum) for the peaks assigned to the 1470 cm^{-1} vibration, and no detectable shift for the others. In the IR spectrum of the CO_3^- ground electronic state, Jacox and Milligan[7] observed shifts of 33 and 42 cm^{-1}, respectively, for the 1307 and 1494 cm^{-1} vibrational quanta; they identified these shifts as the two carbon-oxygen stretching fundamentals. The small shifts observed here, however, are more consistent with bending mode characteristics.

IV. IDENTIFICATION OF THE EXCITED STATE

The expected electron configurations of the ground and first four excited states of CO_3^- are discussed in some detail in Refs. 4, 8, and 9. The ground state is generally agreed to be a 1^2B_2 state, and both XHMO and INDO calculations[9] predict that the odd electron is in a $4b_2$ orbital, which is largely antibonding for the two symmetry-equivalent oxygen atoms. The lowest lying excited states are 2^2B_2, 1^2A_1, 1^2B_1, and 1^2A_2. There should thus be four low-lying transitions:

$$2^2B_2 \leftarrow 1^2B_2 \qquad \text{Z polarized} \qquad (3a)$$

$$1^2A_1 \leftarrow 1^2B_2 \qquad \text{Y polarized} \qquad (3b)$$

$$1^2B_1 \leftarrow 1^2B_2 \qquad \text{forbidden} \qquad (3c)$$

$$1^2A_2 \leftarrow 1^2B_2 \qquad \text{X polarized} \qquad (3d)$$

for which the polarization of the radiation absorbed or emitted is given with respect to the coordinate system in Fig. 2.

Transitions (3c) and (3d) are degenerate for D_{3h} symmetry, and since (3c) is dipole forbidden, (3d) might be expected to be weak. Transitions (3a) and (3b) are also degenerate for D_{3h}, but strongly allowed. Chantry et al.[4] attributed absorption bands (polarized in the plane of the ion) at 5300 Å in CO_3^- and at 6100 Å in the isoelectronic molecule NO_3 to either transition (3a) or (3b), while assigning a transition at 3280 Å for NO_3 to (3d). The calculations of Olsen and Burnelle[9] predict transition (3a) to lie lowest, and that this transition is unlikely to result in a substantial change in the geometry of the system.

The calculations also predict that transition (3b) is next in energy and probably very close to (3a). Further, this transition should result in a substantial change in the geometry of the system, particularly in the angle α, which would produce a photoexcitation spectrum well developed in bending mode structure. It appears reasonable from these calculations that, after a vertical transition to the 1^2A_1 state at the ground state equilibrium value of α (110° in the XHMO calculation, 82° in the INDO), the molecule can undergo bending vibrations during which the angle α approaches 180°. Since the $2^2B_2 \leftarrow 1^2B_2$ vertical transition should not substantially change α, identification of the observed vibrational structure in the photodissociation cross section with this 1^2A_1 state appears most reasonable.

One way to distinguish between transitions (3a) and (3b) in our experiment is by the dependence of the detected O^- photofragment current on the orientation of the linearly polarized laser beam. The geometry of our apparatus[17] is such that photofragments ejected along the axis of the drift tube will be detected with higher efficiency than those ejected perpendicular to this axis. Of course, since the photon-ion interaction occurs in the relatively high pressure drift region, subsequent collisions may decrease the observed polarization effect. However, at the pressure of 0.050 torr at which the experiments reported here were performed, the ions can undergo on the average only three or four collisions before detection. We therefore attempted to observe a polarization effect on the detection efficiency of the O^- photofragments.

The results of this experiment are presented in Fig. 4, where the ratio of the detected O^- photofragment currents (normalized to the same photon flux) for the radiation polarized perpendicular and parallel to the drift tube axis is plotted versus wavelength. For transition (3a), we would expect the ratio $(O^-_\perp/O^-_\parallel)$ to be less than 1; for transition (3b), it should be greater than 1. The result is clearly $(O^-_\perp/O^-_\parallel) > 1$, favoring the assignment of transition (3b). We should point out that transition (3d) would also be expected to yield $(O^-_\perp/O^-_\parallel) > 1$, but other evidence already discussed indicates that the state responsible for the observed structure is not the 1^2A_2.

We thus conclude that the state responsible for the structure observed in the photodissociation cross section is the 1^2A_1, which has its origin 1.520 eV (12260 cm^{-1}) above the origin of the ground state and has three vibrational modes with energies of 990 cm^{-1}, 1470 cm^{-1}, and 880 cm^{-1}. All three of these vibrations probably represent bending modes of the ion in this state. Stretching modes may occur in the absorption spectrum, but may appear only weakly or not at all in the dissociation spectrum.

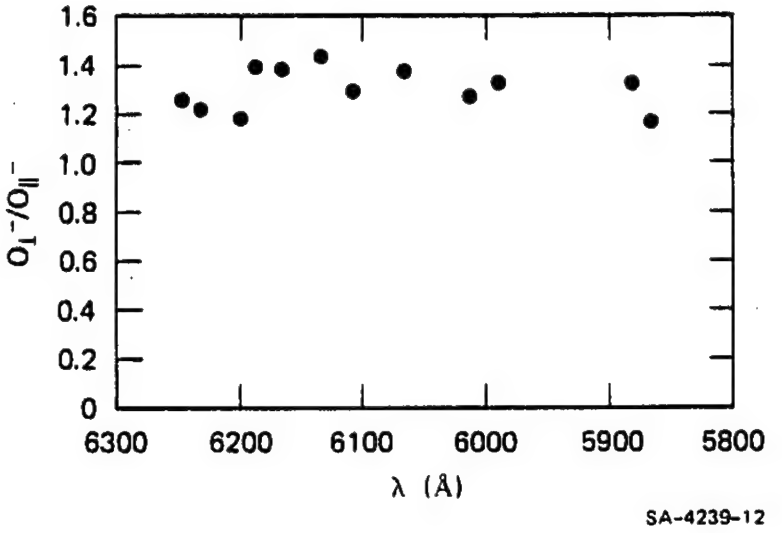

Figure 4. Ratio of the O^- photofragment ions detected when the electric vector of the laser was perpendicular to the CO_3^- drift velocity to those O^- photofragment ions detected when the electric vector was parallel to the CO_3^- drift velocity, plotted as a function of wavelength.

V. OTHER OBSERVATIONS

The absolute cross sections presented in Fig. 1 were determined by observing the disappearance of CO_3^-, as discussed in Refs. 16 and 17. We have also observed[17,18] the appearance of O^- photofragments over the same range of photon energies. Because of the polarization effects discussed in the previous section, and other possible detector discrimination effects, it is not straightforward to relate the observed O^- photofragment current directly to the absolute photodissociation cross section.

Between 1.97 and 2.16 eV, the number of O^- photofragments detected was in excellent agreement[18] with that expected from the cross section as determined from the disappearance of CO_3^-. This was consistent with our assignment of the structure in this region to a perpendicular transition to the 1^2A_1 state. Between 2.41 and 2.59 eV, however, the O^- photofragment current exhibited[17] behavior substantially different from that of the photodestruction cross section. In particular (see Figures 2 and 3 of Ref. 17), photofragments for wavelengths between 2.53 and 2.71 eV were collected with much higher efficiency than those for wavelengths between 2.41 and 2.53 eV when the polarization of the laser beam was oriented perpendicular to the drift tube axis. One possible explanation for this effect, proposed in Ref. 17, is that the two wavelength regions correspond to photodissociation from two excited states of different symmetry. In this model, the 2.41-2.53 eV region would correspond to a parallel

transition since the photofragments are not collected efficiently, while the 2.53-2.71 eV region would correspond to a perpendicular transition, such as in the 1.97-2.16 eV region.

This explanation fits well with transitions (3a) and (3d). Theory[9] predicts that the 2^2B_2 state lies below the 1^2A_2 and that transition (3d) would occur at 2.7 eV. The polarization characteristics of transitions to these states are such that (3a) is a parallel transition, whereas (3d) is perpendicular. Thus it is possible that the photodissociation observed between 2.32 and 2.53 eV arises primarily from transition (3a) and that the photodissociation between 2.53 and 2.71 eV arises from (3d). Recent work by Vestal, Mauclaire, and Futrell[22] indicates that the photodissociation cross section has a maximum near 2.7 eV. This may be fortuitous agreement with theoretical prediction for transition (3d), but it does support the suggestion that the photodissociation between 2.53 and 2.71 eV is due primarily to transition (3d).

These conclusions regarding the assignment of transitions (3a) and (3d) are only tentative. They can be tested by further studies of the polarization and wavelength dependence of the cross section. Photofragment energy distributions[23,24] should also be studied to fully characterize these excited states.

VI. BOND ENERGY AND ELECTRON AFFINITY

The photodissociation of CO_3^- is initiated by photoabsorption, which is a "vertical" transition from the ground state equilibrium configuration of the ion. The threshold for photodissociation can therefore be only an upper limit to the adiabatic dissociation limit or true CO_2-O^- bond energy, $D(CO_2\text{-}O^-)$. As shown in Fig. 3, we observe a strong dissociation peak at 1.85 eV, but note that dissociation also occurs weakly at 1.8 eV and possibly at even lower energies. Since our studies show that the 1.85 eV peak is not influenced by vibrational excitation of the ground CO_3^- electronic state, we regard 1.85 eV as an <u>upper limit</u> to $D(CO_2\text{-}O^-)$.

On the other hand, from the exothermicity of the reaction

$$O_3^- + CO_2 \rightarrow CO_3^- + O_2 \quad , \tag{4}$$

obtained from the equilibrium constant, Ferguson, Fehsenfeld, and Phelps[25] have determined a <u>lower limit</u> of 2.0 ± 0.2 eV for the bond energy $D(CO_2\text{-}O^-)$. We conclude that the bond energy $D(CO_2\text{-}O^-)$ must in fact be very close to 1.80 eV. Thus, the range 1.8 ± 0.1 eV seems almost certain to encompass $D(CO_2\text{-}O^-)$.

Given this value of the bond energy, the electron affinity of CO_3 can be calculated from

$$EA(CO_3) = D(CO_2\text{-}O^-) + EA(O) - D(CO_2\text{-}O^-) \quad . \tag{5}$$

Using $EA(O) = 1.462$ eV[26] and $D(CO_2\text{-}O) = 0.4 \pm 0.2$ eV,[27] we obtain $EA(CO_2) = 2.9 \pm 0.3$ eV. This value is consistent with our previous

conclusion[17] that the primary photodestruction mechanism at 2.71 eV (4579 Å) is photodissociation, not photodetachment. It is in conflict with the value of 1.8 eV for the electron affinity reported by Burt,[15] but it is now clear that photodissociation, not photodetachment, produced the photodestruction observed in his experiment. Hong, Woo, and Helmy[16] recently reported a measurement of the vertical detachment energy of CO_3^-, yielding a threshold of 2.69 ± 0.1 eV, which is consistent with that calculated from Eq. (5).

VII. SUMMARY

The photodissociation cross section of CO_3^- ions having a 300°K distribution of internal states has been measured at wavelengths between 4579 and 6940 Å. The cross section exhibits detailed structure at photon energies between 1.85 and 2.35 eV, characteristic of transitions to vibrational levels of an excited electronic state that predissociates to form O^- and CO_2. The major features of the cross section are single photon absorptions from the ground vibrational levels of the CO_3^- 1^2B_2 ground electronic state. The polarization dependence of the O^- photofragments supports identification of the predissociating state as the 1^2A_1. Three vibrational modes of this state are identified, having frequencies of 900 cm^{-1}, 1470 cm^{-1}, and 880 cm^{-1}. The small isotopic shifts observed in these frequencies for $^{13}CO_3^-$ suggest their assignment to bending modes.

On the basis of these vibrational assignments, the origin of the 1^2A_1 state is predicted to occur 1.520 eV above the ground state. The present observations, together with other measurements, show the CO_3^- dissociation energy, $D(CO_2\text{-}O^-)$, and the CO_3 electron affinity to be 1.8 ± 0.1 eV and 2.9 ± 0.3 eV, respectively.

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